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IMPROVEMENT OF WOOL FIBRES BY REMOVING EXOCUTICLE

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SYNOPSIS

Taking advantage of its susceptibility to change, a process for denaturing non-keratinous protein (NKP) was devised.

Wool was dipped into an aqueous solution at room temperature containing an extremely small amount of an electrophilic agent such as a heavy metal ion¹, and then mechanical action such as twisting was applied repeatedly for a couple of minutes. Swelling of NKP in the lacuna between the cuticle (CU) and cortex (Cx), where the solution penetrated first, was stimulated due to metal complex formation. NKP became compact and hydrophobic and, therefore, its stability was improved. Coordinated metal functioning in electron transfer was localised on and near the surface of the denatured active portions of NKP². Upon chlorination of the wool treated in the manner mentioned above, the keratin on the outermost layer, or exo-cuticle (Ex), alone peeled off because of an instantaneous catalysed oxidation reaction. The adducted metal could be ionised again through oxidation and H⁺ generated, and the metal ion was then washed away. In this way, with a help of a small amount of heavy metal, wool could be changed into metal-functioning protein, like an enzyme.

INTRODUCTION

Generally speaking, the protein constituting the wool fibre is based on a primary structure where a variety of amino acids are linked to form polypeptides. The α -helix structure is held and assembled as a higher ordered stereostructure. Only when its original stereostructure is maintained, can characteristic functions of this protein be demonstrated.

The higher ordered structure is maintained by relatively weak force such as hydrogen bonds, coulombic forces, hydrophobic bonds and Van der Waals force. Under the action of heat, acid, alkali and electrolyte, the molecular assembly is dissolved and the structure is deformed, resulting in it losing its characteristic functions.

The disulphide (SS) bond is responsible for holding the stereo-structure of the protein against mechanical action. The mechanical strength and elasticity of the protein depend on the number of SS bonds.

As is shown in the cross-section stained with silver (Fig. 1 and Table I), wool primarily consists of keratin which contains many SS bonds, or cystine and which is stable mechanically and chemically.



Fig. 1. Cross-section of untreated wool fibre, staining with Ag^3

Table I. Cystine Contents and Swelling Factors^{4,5}

Components		1/2 Cystine	Swelling factor
	Exocuticle	19.9	0.9
	⊙ Endocuticle	3.1	9.0
	⊙ CMC δ-layer	1.3	21.5
	Cortex poor	6.8	5.0
	rich	17.9	1.1

⊙ = non-keratinous protein (NKP)

The keratins are combined with non-keratinous material which contains little cystine and is unstable. Wool composed of different kinds of protein, consists of spindle shaped cortical cells that are assembled parallel to the fibre axis to form a long cylinder. The flat CU surrounds the Cx protectively.

The cell membrane complex (CMC) connecting NKP of each cell in the wool fibre is the only continuous layer in the wool. The NKP carries many anionic as well as cationic amino acid side chains and is called the δ -layer. This lies between lipid membranes, called the β -layer.

The CMC serves as a water-channel. Selective diffusion of various reagents is allowed through these channels. Damage starts at this outermost layer of the wool fibre⁶.

The CMC has strong influences on mechanical and chemical aspects of wool such as crimp formation and setting behaviour⁷. The CMC is damaged by chemical treatments such as scouring, carbonising, shrink-proofing, dyeing, and bleaching that are essential manufacturing processes⁸. It has been considered impossible to prepare wool products without damaging the fine structure of wool.

The phenomenon of felting is attributable to NKP of the CU which is amenable to change. Taking advantage of this susceptibility to change, experiments have been conducted to denature the protein and change the functions that would induce electron transfer in other compounds.

The basis of the treatments was as follows:

1. When protein is immersed in a medium of high dielectric constant such as water, weak inter-chain bonds are destroyed and hydration and swelling occur. When water is removed, the original structure of protein is restored. In the presence of heavy metal ions which form adducts to protein, these weak bonds are not reformed, therefore the original structure cannot be restored easily. In the case of high ionic concentrations of

metal ions, an ordered structure of liquid water is formed and this prevents the protein from hydrating. It is, therefore, necessary to use test solutions of low concentrations of metal that do not affect the hydration and swelling of the protein.

2. An intermediate Lewis acid, Ni^{2+} , was chosen as the heavy metal for these experiments.
3. The largest gap will be formed in the lacuna between CU and Cx, when mechanical treatment such as twisting is applied to the fibre⁹.

When the above-mentioned conditions are met, only the structure of NKP collapses, and hydration and swelling occurs. When the above-mentioned steps are taken repeatedly over a period of minutes, the highly ordered structure of NKP is maintained. With chemical treatment such as chlorination, CMC between Cx will be completely protected, while keratin in the outermost layer, or Ex will easily be peeled off.

The theoretical background for removing Ex has been reported at a previous conference in this series¹⁰.

Remarkable products utilising the exfoliation process have now been established in the market, with industrial rights being granted to major advanced nations¹¹. One of our products is Vantean wool.

EXPERIMENTAL

Material: Australian merino top (mean fineness 22.0 μ) was selected. This was a) untreated wool.

Equipment: Dipping tank equipped with a compound roller having an uneven surface that operates under water.

Treatment: After the top sample was strained, it was dipped into the tank of softened water at 25°C containing 36 ppm of nickel as NiCl_2 . The sample was passed over the roller eight times for approximately 90 seconds to shrink the fibres. It was then washed

in water, passing the roller four times for 60 seconds and dried. This was b) metal adduct wool.

The above mentioned sample was dipped into a 20°C aqueous solution of hypochlorous acid containing 4% o.w.f. of available chlorine, adjusted to pH 4.0 by hydrochloric acid, at a liquor ratio of 15:1 for approximately 8 seconds. It was washed in water, passed through an antichlor bath containing sodium bisulphite and soda ash designed to neutralise the acid, washed in cold water and warm water and then dried.

Microscopical examination showed that Ex of wool fibres was completely peeled off. This was c) Ex removed wool.

Test-1: Among a) untreated wool, b) metal-adduct wool and c) Ex-removed wool, metals were detected in a) and c) by X-ray fluorescence spectroscopy.

Test-2: Based on the outcome of Test-1, all three samples a), b) and c) were wet ashed with concentrated nitric acid. Concentrations of nickel, copper and zinc were determined by an atomic absorption spectrophotometer (Nippon Jarrel Ash & Co., Ltd., Type AA-782).

Test-3: 3 g each of a), b) and c) were washed with ethyl ether for 4 hours in a Soxhlet extractor, dried in a dryer set at 40°C as a preliminary measure, conditioned in a standard state, and dried for 2 hours at 80°C in a vacuum infrared dryer. Equilibrium moisture was measured.

Test-4: Concentration of Ni^{2+} in the solution was measured by using dimethylglyoxime, or test paper containing the oxime.

Test-5: Cross-sections of wool fibres stained with ammoniacal silver nitrate (Ag), osmium acid, uranyl acetate and lead citrate (UO_2+Pb), respectively, were observed on EM photographs.

Test-6: Conventional properties as such as alkali solubility, UB solubility, tensile strength (gf) and elongation (%) for a) and c) were compared.

RESULTS

Test-1: The result of the X-ray fluorescence spectro-photographs is

shown in Figure 2.

Test-2 and 3: The result is shown in Table II.

Test-4: The concentration of Ni^{2+} in the solution is used as a reference for the concentration in the wool.

Test-5: Figure 3 shows an EM photograph of the cross-section of c) Ex removed wool that was stained with $\text{UO}_2 + \text{Pb}$.

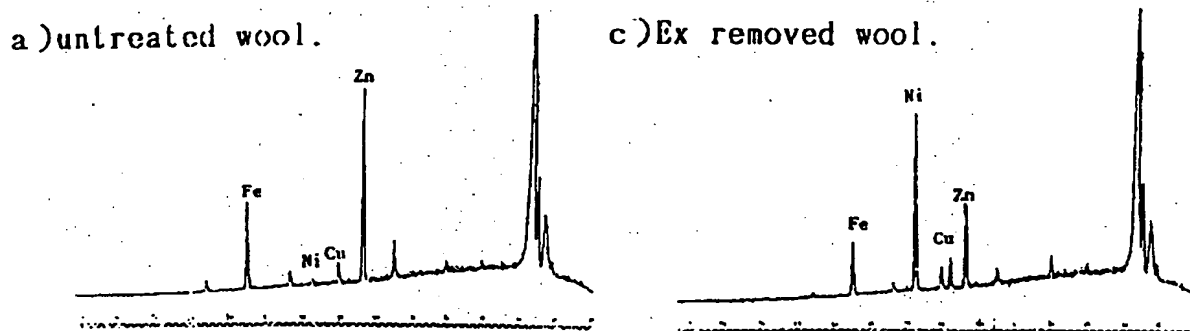


Fig. 2. X-ray fluorescence spectra

Table II. Metal Contents Measured by Atomic Absorption Spectroscopy and Moisture Regains of the Processed Wool

	metal content mg/kg dried wool			moisture regain %
	Cu	Ni	Zn	
a) untreated wool	3.8	0.04	94	15.6
b) Ni adducted wool	3.8	290	92	14.9
c) Ex removed wool	2.7	30	44	14.9

Figure 4 shows the cross-section stained with Ag.

Figure 5 shows an enlarged cross-section of Figure 4.

Test-6: The results are shown in Table III.

DISCUSSION

1. The EM observation of the cross-section stained with Ag to show the high sulphur regions the SS bond (Figs 4 and 5) reveals no conspicuous changes in sample (c) compared with untreated wool. The keratin of the outermost layer, Ex alone, cannot be seen in Figure 5. As reported at the previous conference, it is difficult to conclude that Ex is dissolved, since the content of cysteinic acid

Table III. Effects of Removing Exocuticle

	No.	a) untreated wool	c) Ex removed wool (c - a)/a %
Tensile strength (gf)	1	8.1	8.5 (+5.0)
	2	7.4	7.7 (+4.0)
Elongation (%)	1	45.1	47.9 (+6.2)
	2	45.0	48.0 (+6.6)
Alkali solubility (%)	1	15.3	16.3 (+6.5)
	2	13.6	16.2 (+19.1)
UB solubility (%)	1	46.9	38.3 (-18.3)
	2	37.6	33.0 (-12.2)

after the treatment is small. This indicates that Ex alone is peeled off. The CU has been left unreacted, as can be seen from Figure 3. It is believed that the mechanical action has not affected the part indicated by the arrow and the Ni has not been absorbed at all. Swelling factors are calculated for the NKP part (in Table I), and it has proved the NKP swelled approximately 10 times more the Ex. This figure indicates that the structure has been stabilised due to swelling and formation of chelate bridges.



Fig. 3. Cross-section of c) Ex removed wool stained with UO_2+Pb . (The arrow shows non-reacted CU)

2. Figure 3 shows components unstained with the UO_2+Pb , newly formed on the surface of fibres themselves, or Cx, where the reaction had taken place as expected. This part is confirmed to be

osmophobic. A clear cut outline where staining with Ag can be observed on the surface of Cx is apparent in Figures 4 and 5.

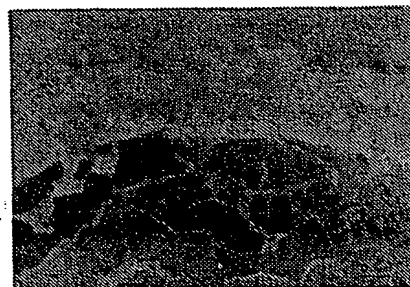
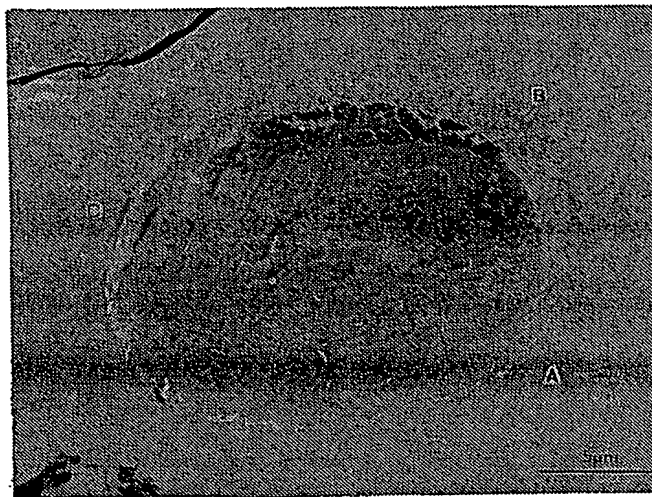


Fig. 5.
Enlarged Fig. 4

Fig. 4. Cross-section of c), Ex removed wool, stained with Ag

Based on the above two observations, this component is believed to be formed when the surface of Cx shrinks and becomes compact in structure.

3. Table II shows that the equilibrium moisture decreases after absorption of metal, but does not change after exfoliation of Ex. It indicates that the NKP on the outer layer of the fibres themselves becomes hydrophobic after absorption of metal¹².

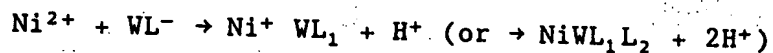
4. The structure of a water channel in the CMC, is not seen around CU in any of the figures. It is believed that the lipid β -layer is also destroyed when the NKP becomes hydrophobic and by mechanical action. Thus, the function of the water channel has collapsed as intended.

5. Table II shows that the metal content of Ni is 290 mg/kg after absorption. Penetration of Ni seems to be difficult under the selected conditions. Distribution of Ni in the formation of an adduct on the surface must be extremely high. Instantaneous decomposition of HOCl is, therefore, reasonable^{10,13}.

6. After the chlorination with HOCl in acidic solution, the concentration of Ni becomes 30 mg/kg. Ni is removed by the oxidation and H^+ ion. Zinc contained in the untreated wool is also removed, therefore the total amount of metal in treated wool is about the same as in untreated wool.

Let us consider the reactions of the NKP with Ni accompanied by mechanical treatment for short time^{14,15}.

1) Ni is effective as an electrophilic agent, and forms an adduct to the looser parts of the NKP of high charge density in a hydration process.



An electronic transfer between metal complexes and ionising parts of NKP changes the structure and causes changes in the properties of wool.

2) Ni decreases the charge density of hydrophilic NKP and loosens the protein structure and also disrupts the lipid β -layer structure.

3) Chelate formation after swelling changes the NKP into more compact protein and makes NKP more mechanically and chemically stable.

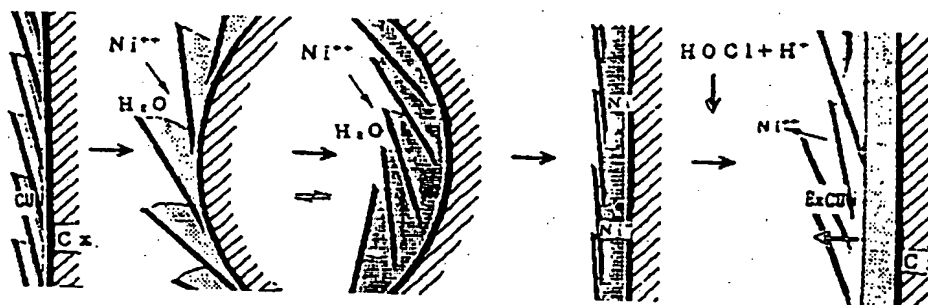


Fig. 6. Speculation of the changes in the outer layers under this process, where NKP is swollen and Ni is adducted to NKP promptly with mechanical action in water

4) The electric potential of the metal ion depends on the bond strength of the ligands. $\text{Ni} \rightarrow \text{Ni}^{2+}$ in acidic solution has an elevated oxidation potential and produces large oxidising forces on the surface of the adducted NKP.

5) Chlorination with HOCl will be catalysed with the generation of Cl^- and the reaction $\text{HOCl} \rightarrow \text{HCl} + 1/2 \text{O}_2$ will be accelerated. As in Figure 6, it is assumed that the swelling and subsequent restructuring of the part surrounded by solid keratin will help tighten Cx but swell Ex. It also helps to compress the keratin of Cx and Ex and to improve the adhesion of CMC between Cxs. Thus hydration and swelling are suppressed, and the CMC prevents water from penetrating into fibres themselves.

The water-channel, or the δ -layer, which is surrounded by the lipid β -layers and swells towards inside of fibres, seems to have an amorphous form that causes isotropic swelling.

As a result, Ex can easily be peeled off with the shock generated by the chlorination and becomes as shown in Figures 3 and 4.

By denaturing NKP in the coordination sphere where heavy metal is adducted, NKP on the outer layer turns into a mediator for the electron transfer. Wool has, thus, been improved into completely shrinkproof fibres for clothing materials, retaining the efficient fundamental functions for crimp formation and setting.

The hydration and dehydration velocities of treated wool become very rapid in comparison with untreated wool.

Friction-generated electrostatic voltage and its half life period drop to a half or one-third of those for untreated wool¹⁶. This indicates that substantial changes in electrical and chemical properties occur. It is also reported that the comfort of clothing from treated wool both for resting and exercising, is better than that of untreated wool or cotton materials¹⁷.

This article has dealt the removal of Ex by oxidation reaction, after adduction of the functional parts of wool with heavy metal and turning it into mediator for rapid reactions.

This method is a remarkably effective pretreatment for permanent waving, hair dyeing, setting of wool fabrics, dyeing with vat dyes that accompany electron transfer (redox) of keratinous fibres. The treatment is confirmed to maintain strength¹⁸.

CONCLUSION

The natural properties of wool are easily damaged. Such damage is unavoidable during the production of apparel fabrics. It has been found, however, that weak points or sensitivities of NKP can be

changed by the assistance of a radical reaction, with heavy metal of similar concentration to that present in nature and then by mechanical action for a couple of minutes, at room temperature in neutral solution. It has also been found that wool, which has favourable forms for practical applications, may be made more functional. Without damaging its properties it may be converted to powerful biological material.

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